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GAS-PHASE OXIDATION OF ALUMINUM ATOMS

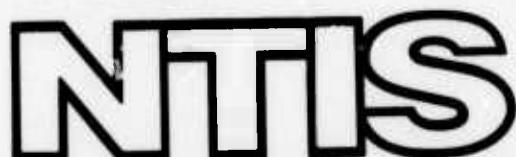
Columbia University

Prepared for:

Advanced Research Projects Agency

1974

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FINAL REPORT

ARPA Order Number 1482, Am. 7
Program Element Code: 62301E

Name of Grantee:
Columbia University
New York, New York 10027

Effective Date of Grant:
May 1, 1973 - April 30, 1974

Grant Number:
DA-ARO-D-31-124-73-G82

Amount of Grant:
\$35,000.00

Principal Investigator:
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(212) 280-2017

Short Title of Work:
Gas-Phase Oxidation of Aluminum Atoms

Sponsored by:
Advanced Research Projects Agency
ARPA Order No. 1482, Am. 7

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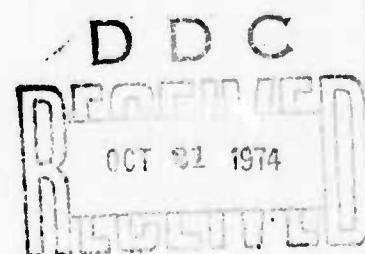


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Statement of Problem

- 1) To investigate the gas-phase reaction



and determine relevant properties of this reaction and of the
AlO high-temperature species of interest to ARPA.

- 2) To investigate the gas-phase combustion of trimethyl
aluminum (TMA) and related metal organics in order to elucidate
mechanism with respect to artificial release of TMA.

Results and Conclusions

Using a beam-gas arrangement,¹ the reaction $\text{Al} + \text{O}_2 \rightarrow \text{AlO} + \text{O}$ ² was investigated by the method of laser-induced fluorescence. The blue-green bands of AlO permitted easy detection of this reaction product and well-developed excitation spectra were obtained under single-collision conditions. From these excitation spectra, relative rotational and vibrational populations are derived for v=0 and v=1. The rotational distributions are found to differ significantly, with v=0 having more rotational excitation than v=1. The vibrational distribution does not fit a temperature, the falloff with v exceeding v=1 compared to v=0. A comparison of the observed internal state distribution to those calculated from phase space theory³ suggests that the breakup of the AlO₂ reaction complex is not governed solely by statistical considerations.

At first glance, this may seem surprising in view of the fact that AlO₂ is a known, stable, high-temperature molecule. However, AlO₂ is expected to have a linear O-Al-O structure, in analogy with BO₂. Hence, it would be very difficult for the Al + O₂ reaction to proceed through this intermediate which requires the insertion of an Al atom between the two O atoms. Although the

molecule Al-O₂ may have bound states, our results suggest that the Al + O₂ reaction most probably proceeds, at least in part, by a direct mechanism. These tentative conclusions can be tested by future measurement of an AlO angular distribution or by further laser-induced fluorescence studies using a velocity-selected Al beam to narrow the large spread in the initial translational energy of the reactants. The present information on the internal state distribution of the AlO products complements the kinetic studies of Fontijn, Felder, and Houghton.⁴ These workers found that the Al + O₂ reaction proceeds with a rate coefficient of $3 \pm 2 \times 10^{-11}$ ml molecule⁻¹ sec⁻¹ which shows no measurable temperature variation over the range 1000-1700 °K. All present results also are consistent with the conclusion that the Al + O₂ reaction has no activation energy.

From a knowledge of the energy partitioning in the Al + O₂ reaction, we are able to set a lower bound on the ground state dissociation energy of AlO, D₀^o(AlO). When this is combined with the upper bound on D₀^o(AlO) found from the long wavelength onset of an AlO absorption continuum, we conclude that

$$D_0^o(\text{AlO}) = 121.5 \pm 1 \text{ kcal/mole} .$$

We believe this provides a solution to a long standing problem which has vexed those interested in the thermodynamic properties, particularly the bond energy, of aluminum monoxide.

Direct measurement of the fluorescence decay of the AlO B $^2\Sigma^+$ state as a function of time permits the radiative lifetime to be determined. We find for the various upper state vibrational levels

$$\tau(v=0) = 100 \pm 7 \text{ nsec}$$

$$\tau(v=1) = 102 \pm 7 \text{ nsec}$$

$$\tau(v=2) = 102 \pm 4 \text{ nsec}$$

where the error estimates represent three standard deviations. Our results are close to those of Johnson, Capelle, and Broida,⁵ who report 128.6 ± 6.0 nsec, but differ markedly from those of Wentink, Pedersen, and Diebold⁶ who report 272 ± 14 nsec. While the 30% disagreement between the work of Johnson et al. and our own is about a factor of two larger than our combined errors, we feel that our results taken with that of Johnson et al. should give confidence to other workers in this field that the elusive electronic lifetime of AlO is now known to an accuracy of better

than a factor of 1.5 (most pessimistic estimate).

The reactions of TMA and TEA (triethyl aluminum) with O₃ were studied at low pressure in a beam-gas arrangement. For TMA the resulting chemiluminescence observed through a 1-m spectrometer showed continuum features as seen previously by us¹ in the reaction Al + O₃, but no AlO emission. However, AlO bands could be excited in fluorescence either by a laser or by a white light source. In the case of TEA, no visible chemiluminescence appeared under identical operating conditions. We do not feel our present results allow us to reach a mechanistic understanding of the combustion of TMA or TEA, but it would appear that several reaction steps are involved. This is consistent with the findings of Linevsky and Alyea.⁷ We also note that while TMA and TEA are pyrophoric liquids, the gas-phase combustion with O₃ in our pressure range produces no visible emission.

References

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Publications Supported by DA-ARO-D-31-124-73-G82

"Fluorescence of Free Radicals: A Method for Determining Dissociation Energy Limits" by R. N. Zare which appeared in Berichte der Bunsen-Gesellschaft für physikalische Chemie 2, 153 (1974).

"Laser Fluorescence Study of AlO Formed in the Reaction Al + O₂: Product State Distribution, Dissociation Energy, and Radiative Lifetime" by P. J. Dagdigian, H. W. Cruse, and R. N. Zare which has been submitted to the Journal of Chemical Physics for publication.